TABLE IV

EFFECT OF TEMPERATURE ON POLARIZATION RESISTANCE AND CAPACITANCE, SMOOTH PLATINUM ELECTRODES IN 0.1 N $Ni(NO_3)_2$

f	C_P $\mu\mu$f	R_S	C_S, μf	ΔR	$C_S\sqrt{\omega} \times 10^6$	$\Delta R C_S \omega = \tan\psi$	$\frac{dC_q}{C_{S25}dT}$	$\frac{d\Delta R}{R_{25}dT}$
		0°						
500	10,073	579.33	29.96	4.89	1679	0.460		
1000	2823	577.72	26.88	3.28	2131	.554		
2000	820	576.75	23.22	2.40	2603	.700		
3000	388	576.42	21.83	1.98	2997	.812		
4000	231	576.25	20.64	1.81	3272	.939		
		25°						
500	24,010	326.91	39.46	3.81	2212	0.472	0.0096	−0.011
1000	7232	325.77	33.00	2.67	2616	.554	.0074	− .009
2000	2171	324.94	27.62	1.84	3096	.639	.0064	− .010
3000	1055	324.65	25.31	1.55	3475	.740	.0055	− .011
4000	640	324.50	23.49	1.39	3724	.821	.0049	− .012

These results are satisfactorily expressed by the equations $R_S = 574.44 + 269/\sqrt{\omega}$, at 0°, and $R_S = 323.10 + 212/\sqrt{\omega}$, at 25°.

In this case the temperature coefficient of the polarization resistance is negative and about 1% per degree and independent of the frequency. The temperature coefficient of the capacitance is positive but varies from about 1% at 500 cycles to about 0.5% at 4000 cycles.

Summary

1. A new form of cell suitable for measuring the resistance and the capacitance due to galvanic polarization with alternating current has been devised and used for a series of measurements with silver, nickel and platinum electrodes.

2. Polarization resistance is inversely proportional to the square root of the frequency. Another method of measuring polarization resistance based on this law is described.

3. Polarization causes a capacitance in series with the resistance which decreases with increasing frequency.

4. Both polarization resistance and polarization capacitance are greatly dependent on the metal used for the electrodes, and dependent to a lesser degree on the electrolyte and temperature, but independent of the current density and the separation of the electrodes and uninfluenced by another superimposed current of a different frequency.

CAMBRIDGE, MASS. RECEIVED SEPTEMBER 27, 1934

[CONTRIBUTION FROM THE BYERLY CHEMICAL LABORATORY OF RADCLIFFE COLLEGE]

The Measurement of the Conductance of Electrolytes. VII. On Platinization[1]

BY GRINNELL JONES AND DOROTHY M. BOLLINGER

Introduction

Kohlrausch[2] discovered that errors due to polarization in the measurement of the conductance can be minimized by covering the electrodes by a deposit of finely divided black platinum. He recommended deposition of the platinum by electrolysis from a solution of chloroplatinic acid (H_2PtCl_6) to which a trace of lead acetate has been added. Nearly all later investigators in this field have used platinized electrodes prepared as recommended by Kohlrausch except when using very dilute solutions or when there was a danger that the platinum black might catalyze an undesired reaction in the solution. A detailed review of the earlier studies[3] of the effect of platinization must be omitted for the sake of brevity.

The purpose of this investigation was to develop a convenient and reliable quantitative test of the quality and sufficiency of the platinization and to use it for a critical study of the procedure of platinization. The adequacy of platinization has been judged by the earlier investigators by one or more of the following tests: (1) the sharpness of the minimum of sound in the telephones and the identity of pitch on opposite sides of the minimum; (2) intercomparisons of two or more cells with a series of identical solutions; (3) the magnitude of reactance due to polarization, or some related quantity such as the capacitance or

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[1] The earlier papers in this series are: Grinnell Jones and R. C. Josephs, THIS JOURNAL, **50**, 1049 (1928); Grinnell Jones and Giles M. Bollinger, *ibid.*, **51**, 2407 (1929); **53**, 411 (1931); **53**, 1207 (1931); Grinnell Jones and B. C. Bradshaw, *ibid.*, **55**, 1780 (1933); Grinnell Jones and S. M. Christian, *ibid.*, **57**, 272 (1935). This investigation was started in the laboratory of Bowdoin College by the late Giles M. Bollinger with the aid of Dorothy M. Bollinger. After the death of Professor Bollinger the work was transferred to Radcliffe College.

[2] F. Kohlrausch, *Wied. Ann.*, **60**, 315 (1897); F. Kohlrausch and L. Holborn, "Das Leitvermögen der Elektrolyte," published by Teubner, Leipzig, p. 9, 1898.

[3] M. Wien, *Wied. Ann. Physik*, **58**, 46, 56 (1896); *Drude Ann. Physik*, **8**, 373 (1902); Whetham, *Phil. Trans.*, **194**, 321 (1900); P. Schönherr, *Drude Ann. Physik*, **6**, 116 (1901); E. Warburg, *Drude Ann. Physik*, **6**, 125 (1901); W. A. Taylor and H. L. Curtis, *Phys. Rev.*, [2] **6**, 61 (1915); W. A. Taylor and S. F. Acree, THIS JOURNAL, **38**, 2409, 2421 (1916); E. W. Washburn, *ibid.*, **38**, 2456 (1916); H. C. Parker, *ibid.*, **45**, 1366 (1923); Grinnell Jones and Giles M. Bollinger, *ibid.*, **53**, 411 (1931); Grinnell Jones and S. M. Christian, *ibid.*, **57**, 278 (1935).

inductance required to obtain a balance, or the phase displacement across the cell.

The first test fails completely with modern single-frequency pure sine wave oscillators. The second test is laborious and inconvenient. The third test is difficult to interpret because the parallel capacitance, which is what is usually measured, as well as the quantities which may be derived from it by computation, depends on the resistance being measured and the frequency as well as on the quality of the platinization. None of these tests give a quantitative measure of the error due to polarization and therefore they do not enable the experimenter to be sure that the error is negligible for his purposes, or to compute a correction if the error is not negligible.

Jones and Christian found experimentally that the polarization resistance is always positive in spite of considerable variations in the nature of the electrodes, the nature and concentration of the solutions, the frequency and the temperature. No evidence that polarization can cause a decrease in resistance under any conditions was found. They also give proof of Warburg's law that polarization resistance is inversely proportional to the square root of the frequency within the audio range. A test of the effectiveness of the platinization may be based on this law. We may write $R_S = R_T + k/\sqrt{\omega}$; where R_S is the measured or apparent resistance of the cell and R_T is the true resistance of the electrolyte with error due to polarization eliminated. Therefore if we plot the measured resistance against the reciprocal of the square root of the frequency we should get a straight line provided the other causes for variation of resistance with frequency have been eliminated. The intercept of this line on the axis of the resistance should give the true resistance. The difference between the apparent resistance and the true resistance as thus determined gives the error due to polarization. This error will be dependent on the frequency and on the quality of the platinization and possibly on other factors. If the error as thus determined is insignificant the platinization is adequate and no correction needs to be applied to the measured resistance to give the true resistance. With modern vacuum tube oscillators the frequency can be altered by merely turning a dial or rotating a multiple switch and therefore the resistance can be measured with several frequencies almost as quickly as it can be measured with a single frequency. The method may therefore be adopted as a part of the routine of conductance measurements with a minimum of inconvenience and delay.

Experimental

The general plan of the experiments was to start with a cell with smooth unplatinized electrodes, fill it with the platinizing solution and mount it in an oil thermostat at 25° and measure the resistance and capacitance with 700, 1000, 1490, 2010 and 3070 cycles per second. Then a direct current of 0.010 ampere was passed through the cell with a reversal of polarity every ten seconds for a total of ten minutes. Thus each electrode acted as cathode while 3 coulombs was passing. Under these conditions very little hydrogen is evolved, so that the amount of platinum deposited can be estimated approximately by Faraday's law of electrolysis. Then after waiting until the temperature had returned to 25°, the resistance and capacitance were again measured at each of the frequencies. Then more platinum was deposited and the readings taken repeatedly in the same manner until the deposit of platinum was abnormally heavy. The frequency used was determined by means of a General Radio wavemeter, their type number 434-B. The frequencies given are probably correct within 2%. The precision of the capacitance measurements on our bridge is much below the precision of the resistance measurements, especially when the reactance is low. Errors of as much as 10 $\mu\mu$f in the value of C_P are possible and therefore values below 20 $\mu\mu$f are not recorded at all. The cells used in all of these experiments were of the type shown in Fig. 14 of the third paper of this series.

Some experiments were carried out with a platinizing solution containing platinum chloride and hydrochloric acid (but no lead acetate). The detailed results of these experiments are omitted for the sake of brevity since the deposit was clearly less satisfactory than those obtained from solutions containing lead acetate. When lead acetate was omitted the deposits were a dull gray but even when quite thick did not acquire the sooty black color characteristic of deposits formed from solutions containing lead acetate. In the early stages of the platinization the results were fairly satisfactory but by the time the total current passed to each electrode amounted to about 6 coulombs the results became erratic. The deposit began to come off in flakes and in one case the entire deposit fell off the electrode in one piece. Our experience confirms the wisdom of Kohlrausch's recommendation to use platinizing solutions containing lead acetate.

A part of the data obtained in one typical experiment are recorded in Table I. Similar data with various intermediate amounts of platinum are omitted for the sake of brevity. The cell used in this experiment had electrodes consisting of circular disks 3 cm. in diameter and mounted 8.5 cm. apart. The narrow part of the cell was 2 cm. in diameter and 4.5 cm. long. The cell constant was about 3. The platinizing solution was 0.025 *N* hydrochloric acid containing also 0.3% of platinum chloride and 0.025% of lead acetate. At the head of each section in the table is given the total number of coulombs received by each electrode as a cathode since the platinization started. Assuming that the current which passes to the back surface of the electrode is negligible, the total coulombs per sq. cm. may be computed by dividing these figures by 7.07. The table gives for each frequency and degree of platinization the resistance and parallel capacitance, C_P, required in the other arm of the bridge to give a balance. The table also gives the value of C_S computed by the method explained in the sixth paper of this series. The value of the true resistance of the electrolyte, R_T, was computed by the use of the equation $R_S = R_T + k/\sqrt{\omega}$ as explained in the previous paper of this series, and the result is shown in the table, opposite the symbol R_T. The polarization resistance was then computed from the relationship $\Delta R = R_S - R_T$. The last column gives the value of $\tan \psi = \Delta R C_S \omega$.

The most conspicuous result of these experiments is the great effect of the first small deposition of platinum in reducing the error in the resistance due to polarization. The polarization resistance on the original smooth electrodes was 4.28 ohms with 1000 cycles, but after only 3 coulombs had been passed to each electrode as a cathode (or about 0.42 coulomb per sq. cm.) the polarization resistance with 1000 cycles had

TABLE I

EFFECT OF PLATINIZATION ON ALTERNATING CURRENT POLARIZATION

f	R_S	C_P μμf	C_S μf	ΔR	$\Delta R C_S \omega = \tan \psi$	R_S	C_P μμf	C_S μf	ΔR	$\Delta R C_S \omega = \tan \psi$
	Platinization 0					Platinization: 42 coulombs/electrode				
700	213.565	25,233	44.9	5.097	1.01	207.031	301	4010	0.007	0.12
1000	212.753	15,309	36.5	4.285	0.98	207.029	147	4020	.005	.15
1490	211.975	8582	29.6	3.507	.97	207.029	57	4670	.005	.22
2010	211.480	5408	25.9	3.012	.99	207.028	21	6970	.004	.35
3070	210.893	2905	20.8	2.425	.97	207.027	..	..	.003	...
4350	210.523	1640	18.4	2.055	1.03					
R_T	208.468					207.024				
	Platinization: 3 coulombs/electrode					Platinization: 90 coulombs/electrode				
700	207.763	1413	848	0.080	0.30	212.588	200	5720	0.007	0.18
1000	207.747	717	819	.064	.33	212.586	99	5670	.005	.21
1490	207.735	326	811	.052	.40	212.586	36	7000	.005	.33
2010	207.729	180	807	.046	.47	212.585	..	..	.004	...
3070	207.722	73	854	.039	.64	212.584	..	..	.003	...
R_T	207.683					212.581				
	Platinization: 6 coulombs/electrode					Platinization: 450 coulombs/electrode				
700	207.062	846	1420	0.035	0.22	206.277	90	13,500	0.008	0.48
1000	207.055	430	1380	.028	.24	206.276	46	13,000	.007	.45
1490	207.050	188	1420	.023	.31	206.275	17	15,800	.006	.89
2010	207.047	100	1460	.020	.37	206.274	..	..	.005	..
3070	207.044	40	1570	.017	.51	206.273	..	..	.004	...
R_T	207.027					206.269				
	Platinization: 12 coulombs/electrode					Platinization: 800 coulombs/electrode				
700	206.373	531	2290	0.019	0.19	194.276	..	..	0.024	..
1000	206.370	267	2230	.016	.22	194.272	85	7900	.020	0.99
1490	206.367	116	2310	.013	.28	194.270	55	5500	.018	.93
2010	206.365	57	2580	.011	.36	194.266	34	4900	.014	.87
3070	206.363	..	..	.009	...	194.263	18	4000	.011	.84
R_T	206.354					194.252				

dropped to 0.064 ohm. The amount of platinum responsible for this effect was only 0.2 mg. per square centimeter of electrode surface (assuming that it all deposited on the front surface). This amount is barely detectable by visual inspection as a slight tarnish. Further depositions of platinum caused a steady but much smaller improvement until 42 coulombs had been passed per electrode (about 6 coulombs per sq. cm.) when ΔR with 1000 cycles was reduced to a minimum of 0.005 ohm. Then the value of ΔR remained unchanged while the total platinum deposited was more than doubled and then began a slight rise. The table also shows that the platinization caused a great decrease in C_{P} and an increase in C_{S} which also is relatively greater for the first portion of platinum deposited. However, the maximum in C_{S} was found only after 450 coulombs had been passed per electrode. In this case more than ten times as much platinum was required to give a maximum series capacitance (or minimum reactance) as was required to give a minimum polarization resistance. This experiment indicates that with excessive platinization the quality may be injured as is shown by the rise in ΔR and the decrease in C_{S}. The value of $\tan \psi$ for the unplatinized electrodes was very nearly 1 and independent of the frequency, which is in harmony with the theoretical predictions made by Warburg. Platinization caused a progressive decrease in $\tan \psi$, especially at the lower frequencies, to a minimum when 42 coulombs had passed followed by a rise back to 1 when 800 coulombs passed.

We have made three other similar series of experiments using other cells differing in area of electrodes and cell constant, which confirm the general conclusion stated above, but we refrain for the sake of brevity from publishing the results in detail because a study of the data has failed to reveal any general relationship or tendency not shown in the case reported above, except that none of these other cases give any indications of increasing polarization with excessive platinization. We have no satisfactory explanation of this discrepancy but since it only appears when the platinization is clearly excessive it is of no practical importance.

The best criterion to determine whether or not the platinization is sufficient to eliminate errors due to polarization is the variation of the apparent or measured resistance with frequency, provided other causes for a variation of resistance with frequency have been eliminated. Since it has been demonstrated in the preceding paper of this series and in this investigation that the error in the resistance due to polarization is inversely proportional to the square root of the frequency, it follows that if the resistance is measured successively with two frequencies, one of which is four times the other (say 1000 and 4000 cycles), then the error at the higher frequency will be equal to the difference between the results at the two frequencies. If the error as thus determined is negligible for the purpose of the measurement, then the platinization is adequate. The great virtue of this criterion is that it may be applied easily and quickly as a matter of routine in the course of conductance measurements to ensure that under the conditions of each particular experiment significant errors due to polarization and to several other causes have been avoided. An abnormally high value of the parallel capacitance may serve as a warning to an experienced operator but the interpretation of this warning is not so simple and obvious.

It is impossible to make a general recommendation as to the best degree of platinization because this depends on many variable factors, including the area of the electrodes, the cell constant, the concentration and the chemical nature of the solution to be measured and the precision desired. This investigation, however, has shown that the tendency in the past in this Laboratory has been to overdo the platinization. Very few, if any, experimenters in other laboratories have described their procedure in sufficient detail to permit us to judge whether or not this is commonly true.

If the solutions to be used are neutral and not too dilute (0.01 N or more) and if adequate amounts are available to permit sufficient rinsing and if there is no danger that the platinum black will catalyze a chemical reaction, then sufficient platinum to give a minimum value of the polarization resistance may be used with advantage. The criterion to determine this is the variation of the resistance with frequency as explained above. If the electrodes are of sufficient area and the cell constant large enough the error due to polarization usually can be made negligible by adequate platinization even in work of the highest precision so that no correction to the measured results is necessary.

On the other hand, if the solutions to be measured are either acid or alkaline, or very dilute, or liable to be influenced catalytically by the platinum, it may be advisable to reduce the platinization or even to eliminate it entirely. In this case a correction for the polarization resistance may be determined from the variation of the resistance with the frequency and applied to the results by the use of the equation $\Delta R = R_S - R_T = k/\sqrt{\omega}$.

Summary

1. The various criteria as to the quality and sufficiency of platinization in the measurement of the conductance of electrolytes are discussed and compared; and a test based on the variation of apparent resistance with frequency is recommended.

2. The addition of lead acetate to the platinizing solution, as recommended by Kohlrausch, is helpful.

CAMBRIDGE, MASS.

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[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON]

The Influence of the Concentration and Nature of the Solute on the Compressions of Certain Aqueous Solutions[1]

BY R. E. GIBSON

In continuation of a study of the effect of pressure on solutions,[2] we have determined over the whole range of concentration the compressions to 1000 bars[3] of aqueous solutions of the salts mentioned in Table I. It is the object of this paper to publish the thermodynamic data and call attention to several interesting generalizations which have been found. The apparatus, technique and method of calculating the results have already been described,[2a] but a few modifications made in the course of the work may be mentioned. By immersion of the manganin-wire pressure gage and the comparison coil in a well stirred oil thermostat, it was possible to eliminate a small but troublesome wandering of the zero point, traced to differences in the temperature coefficients of resistance of the two coils and also to avoid corrections for the change with temperature of the pressure coefficient of manganin which in our apparatus amounted to approximately the equivalent of 1 bar per degree at one thousand bars between 22 and 30°.

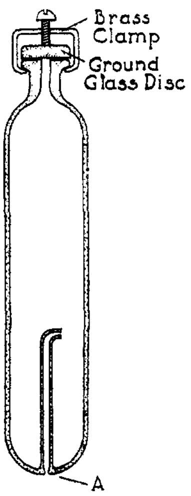

Fig. 1.—Flat-topped piezometer.

As a consequence of this improvement it was possible to make better observations of the freezing pressures of pure benzene, freshly distilled over phosphorus pentoxide, and it was found necessary to modify equation (1) given in the previous paper,[2a] which expressed the freezing pressure of benzene in bars as a quadratic function of the temperature.

$$P = 518.8 + 37.4(t - 20) + 0.104(t - 20)^2 \quad (1)$$

Better values of the freezing pressures of benzene (according to the absolute gage in this Laboratory) are obtained by *subtracting* from the pressures calculated by equation (1) one, two and four bars at 20, 25 and 32°, respectively.

The reproducibility of the piezometers was noticeably improved when the glass stopper was replaced by a flat ground-glass cap (see Fig. 1), and the orifice at A was constricted to a diameter of 0.5 mm. During the work a significant result on the effect of heat treatment on the behavior of a Pyrex glass piezometer under pressure was noticed. A flat-topped piezometer which had not been specially annealed gave us a mean of seven observations 0.03890 for the compression of water, values of 0.00303 and 0.00399 being assumed for the compressions of Pyrex glass and mercury, respectively. The piezometer was heated slowly to 550° in a good furnace, held there for seven minutes, and then allowed to cool slowly. The temperature dropped to 539° in one hour and from 539 to 480° in two and a half hours. The mean of five observations of the compression of water in this piezometer now rose to 0.03916. The difference between these two sets of observations can only be satisfactorily accounted for by

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(1) Read in part before the Division of Physical and Inorganic Chemistry at the meeting of the American Chemical Society in Cleveland, September, 1934.

(2) Gibson, (a) THIS JOURNAL, 56, 4 (1934); (b) *ibid.*, 56, 865 (1934).

(3) To avoid cumbersome repetition the term compression will be used throughout this paper to mean the relative decrease in volume which a phase suffers when its pressure is increased from 1 to 1000 bars.